

SECURITY C

AD-A197 710

DOCUMENTATION PAGE

1a. REPORT

NA

2a. SECURITY

NA

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

NA

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

INDU/DC/GMH/TR-40

6a. NAME OF PERFORMING ORGANIZATION

Indiana University

6b. OFFICE SYMBOL

(If applicable)
NA

1b. RESTRICTIVE MARKINGS

NA

3. DISTRIBUTION/AVAILABILITY OF REPORT

Distribution Unlimited; Approved for
Public Release

5. MONITORING ORGANIZATION REPORT NUMBER(S)

NA

7a. NAME OF MONITORING ORGANIZATION

ONR

6c. ADDRESS (City, State, and ZIP Code)

Department of Chemistry
Bloomington, IN 47405

7b. ADDRESS (City, State, and ZIP Code)

800 N. Quincy Street
Arlington, VA 222178a. NAME OF FUNDING/SPONSORING
ORGANIZATION8b. OFFICE SYMBOL
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

Contract N00014-86-K-0366

8c. ADDRESS (City, State, and ZIP Code)

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.PROJECT
NO.TASK R&T
NO. Code
4134006WORK UNIT
ACCESSION NO

11. TITLE (Include Security Classification)

AAS -- Has it Gone or Where is it Going?

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT

Technical

13b. TIME COVERED

FROM TO

14. DATE OF REPORT (Year, Month, Day)

11 July 1988

15. PAGE COUNT

34

16. SUPPLEMENTARY NOTATION

Accepted for publication in Journal of Analytical Atomic Spectrometry

17. COSATI CODES

FIELD

GROUP

SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Atomic Absorption, Elemental Analysis

19. ABSTRACT: A brief survey of the current literature would suggest that atomic absorption spectrometry is on its way out as an analytical technique. Each year, fewer papers appear that describe novel AAS instrumentation, techniques, or applications. Instead, most studies on atomic spectrometry are concerned with the inductively coupled plasma, alternative plasma sources, or novel means of detection. In this paper, this apparent trend will be considered, the development (or decline) of AAS will be compared to that of competing techniques for elemental analysis, and unusual directions in AAS and similar methods will be reviewed.

Although the number of recently published manuscripts that deal with AAS is indeed declining, the number of AAS determinations performed each year remains substantial. Similarly, sales of AAS instruments remain strong. This trend can be attributed in large measure to the simplicity and convenience of use that surrounds AAS procedures. Also, the sensitivity of furnace/AAS continues to be important in many applications.

Detracting from AAS are its continued and recognized shortcomings as a truly simultaneous multielement method. The necessary straight-line geometry of an absorption process, coupled with the convenience of the hollow cathode lamp as a primary source, make it difficult to adapt AAS to multielement schemes. As a result, complex samples must be run repeatedly for a full elemental profile to be determined. Furthermore, performing qualitative analysis on samples becomes an arduous task by AAS.

Atom cells ordinarily used for AAS also remain one of the method's limitations. Most determinations are currently performed with furnace-based units, and great care must be exercised to avoid interferences which can plague such systems. Clearly, for AAS to remain viable in the face of strong competition from alternative techniques will require novel instrumentation or approaches.

Among the novel concepts that have been introduced are those involving continuum sources and high-resolution spectral-sorting devices, interesting atomization devices, and entirely new detection approaches. The impact of these developments will be evaluated against the backdrop of similarly exciting advances in competing techniques. The date when AAS dies will be predicted.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

Distribution Unlimited

22a. NAME OF RESPONSIBLE INDIVIDUAL

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(812) 335-2189

22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N14-86-K-0366

R&T Code 4134006

TECHNICAL REPORT NO. 40

AAS -- HAS IT GONE OR WHERE IS IT GOING?

by

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Prepared for Publication

in

JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY

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11 July 1988

Accession For	
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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
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Introduction

Atomic absorption spectrometry (AAS) has now been with us, as a recognized analytical method, for some 33 years. As with most methods, AAS has been periodically reviewed, its current status assessed, and projections for the future made. One of the most authoritative treatments was by Sir Alan Walsh (1), who concluded that, in 1974 at least, AAS was still pregnant with promise.

Another, more recent, assessment by Koirttyohann (2) is also especially useful. Other appraisals have been made (3-7) and a number of authoritative reviews have been presented. In 1980 (8) and 1984 (9), entire volumes of the journal *Spectrochimica Acta, Part B* were devoted to AAS and were intended to recognize, respectively, Alan Walsh and Boris L'vov, two of the pioneers in the field.

In these treatments and in others, a number of approaches have been used to gauge and project the growth of AAS. For example, many will recall the prediction by John Willis made in the mid-1960s. John traced the growth of AAS instrument sales and found a nearly exponential increase. Extrapolated to the year 2000, John predicted facetiously that the entire surface of the earth would at that time be covered by AA spectrometers. Although that trend did not change markedly by 1974 (1), sales have now apparently leveled off (6), luckily for us all.

Another way in which the health of a method can be evaluated is by an examination of publications that describe it. L'vov (10) showed that flame AAS publications declined over the period 1970-1982 while AAS papers in which a furnace was employed grew during the same period. Figure 1, derived from citations recovered through Chemical Abstracts, shows that the total number of AAS publications reached a peak in 1983 and now seems to be

in decline. This trend, coupled with the clear prominence of inductively coupled plasma-emission spectrometry and the emergence of ICP-mass spectrometry argues that it is especially appropriate at this time to examine where the field of AAS finds itself and where it might be going.

The "Roots" of AAS

It is not uncommon that treatments of "future perspectives" on a selected topic degenerate into a reminiscence of past events. The present narrative will probably be no exception. Nonetheless, it is appropriate to examine Tables 1-3, which list the many important events that led to the development of AAS as we now know it. From these developments have sprung the strengths and weaknesses of AAS which we now recognize. Knowing these strengths and weaknesses, we can perhaps more confidently extrapolate our current situation into the future.

It is interesting to note that important events in the history of AAS can be divided into at least three categories. Background developments (Table 1) occurred in the period prior to 1930 and involved the characterization of atomic spectra and the introduction of apparatus necessary for performing AAS. A number of "firsts" occurred in the period from 1940-1960 (Table 2) and are responsible for the evolution of atomic absorption as a phenomenon into a truly useful technique for elemental analysis. Since 1960 (Table 3) most of the key events involved the development of improved instrumentation for performing routine AAS. For additional details on these and other important and interesting events in the history of AAS, the reader is referred to the excellent treatment by Koirtzmann (11) and the more general text by Laitinen and Ewing (12).

An Assessment of AAS

It is tempting and certainly not inappropriate to compare AAS to techniques with which it is competitive. However, I believe it is even more useful to compare an analytical method to an ideal standard. If an ideal can be established, it provides a fixed benchmark against which all approaches can be judged. It then becomes possible to gauge how much improvement in particular areas is possible and how much effort should be expended to improve specific features of a technique.

The list compiled in Table 4 is not the only assembly of ideal characteristics that might be offered. Indeed, other authors have published similar lists, many longer or shorter than this one. However, in reviewing any list, one cannot help but be struck by the realization that many of the strengths and shortcomings of AAS derive from the nature of the light source and the atomizer that it customarily employs.

For example, the use of a hollow cathode lamp (HCL) as a light source was central to the success of the original invention of Alan Walsh. Because the HCL emits an extremely narrow band of radiation that is locked onto the resonance lines of the atoms of interest, it provides relatively linear Beers-law plots, minimizes spectral interferences, and makes the alignment of instrumentation and the selection of wavelengths nearly trivial. Yet, the HCL couples with the necessary straight-line geometry of AAS optics to make the technique usable for only one-two-three elements at a time. As a result, the rate of multielement analysis suffers and qualitative analysis becomes impractical.

Similarly, a carbon furnace atomizer, widely employed in AAS, offers extremely high sensitivity in terms of both concentration and mass. Also, because conditions within the furnace can be modeled and predicted

relatively well, it offers the potential for absolute (standardless) analysis (13). Nonetheless, most furnace-based determinations require optimization of conditions for each element (e.g. temperature program, observation time) in order to produce optimal results. Multielement operation is consequently compromised. Also, interelement interferences still plague the technique and background absorption and scattering must be overcome. With few exceptions, furnace and flame atomizers are both limited to the use of solution samples and are capable of atomizing effectively only a fraction of the elements in the periodic table. Finally, limitations imposed by the light source, the atomizer, and the fundamental characteristics of an absorption process itself commonly limit the dynamic range of AAS measurements to two or three orders of magnitude.

Because many of the attractive features of AAS are attributable to the HCL or atomizer, one cannot practically overcome these critical shortcomings just by selecting alternative components. To do so ordinarily generates a host of new inconveniences and drawbacks.

Let us then turn to broader alternatives in an effort to identify an instrumental configuration that might retain the strengths but minimize the failings of current systems. Our approach will be to address one by one the limitations of current AAS systems that were mentioned above. After reviewing our options for overcoming each limitation, we will be able to assess whether any alternative that currently exists will offer significant improvement.

Shortcomings of AAS Related to the HCL

Multielement AAS

In the past, a number of ingenious optical configurations have been proposed to enable HCL-based AAS to be employed in a multielement mode. Most of these schemes, despite their elegance, suffered from substantial light loss or were inordinately complicated. As a result, analytical performance suffered or the systems were judged impractical.

Of course, most AAS instrument manufacturers offer HCL arrangements that permit lamps to be changed rapidly. One supplier (14) even mounts the HCL array in a ferris-wheel like turret that is spun rapidly. In this way, a sequence of elements can be read during each turret rotation.

A more attractive approach, but one which has never been completely successful in a commercial instrument, is the combination of a continuum source and high-resolution spectral dispersion. A commercial system offering this combination was marketed a number of years ago, but never achieved great acceptance, perhaps in part because of its novelty.

A common problem with continuum sources is their relatively low intensity in the ultraviolet region of the spectrum. Also, they must be coupled with a high-resolution monochromator or spectrometer if relatively linear working curves and low detection limits are to be obtained.

Many of the options that exist in continuum-source AAS have recently been reviewed (15). Other possibilities, not reviewed, include the combination of a continuum source and a Fourier-transform spectrometer, the use of an imaging (TV-like) detector with a continuum source and an echelle monochromator, the application of a resonance monochromator as a narrow-band spectral isolation device in continuum-source AAS, and an instrument based on resonance Schlieren (or Hook) spectrometry (16,17) (see Fig.2).

Unfortunately, each of these methods has its own set of limitations. In most configurations (15), there is no intrinsic wavelength lock between a detected spectral band and the atomic transition of interest. As a result, drift in optical components can adversely affect results, and the likelihood of spectral interferences increases. If such problems could be overcome, say, by stabilizing a high-resolution (e.g. echelle) spectrometer or by introducing an internal spectral reference, the most attractive approach to me involves the coupling of a modern charge-injection device (CID) or charge-coupled device (CCD) array photodetector with an echelle-grating spectrometer. Such detector arrays are reportedly capable of single-photon detection, like a photomultiplier tube, but can record and integrate signals from more than 250,000 spectral locations at once (18,19). The result of this combination would be an atomic-absorption spectrometer capable of both multielement and qualitative analysis.

Other alternatives to continuum-source atomic absorption can provide a desired wavelength lock to atomic spectral lines but suffer drawbacks of their own. For example, the selective-line modulation (SLM) approach (20) and a resonance monochromator ordinarily employ optical elements that generate additional noise and worsen both sensitivity and precision. Similarly, Fourier-transform spectrometry is likely to yield poorer signal-to-noise ratios than can currently be obtained with an HCL. Finally, resonance Schlieren or Hook spectrometry, while attractive in their simplicity, would suffer in terms of sensitivity in a comparison with current instrumentation.

A practicable alternative to the foregoing continuum-source options would involve the use of a rapidly scanned, narrow-band primary light source. Unfortunately, the only such device now available is a tunable

laser; such systems are at present costly, temperamental, limited in their wavelength coverage, and cannot be scanned as rapidly as necessary.

If a sufficiently simple, stable, reliable and inexpensive laser source should become available, it could be used in a number of ways besides as a primary light source in a conventional AAS instrument. For example, photothermal or optogalvanic measurements would become more attractive, as would those based on thermally induced gratings (see Fig. 3). These absorption-based measurements would depart substantially from our conventional view of AAS, although they offer certain attractive features. Yet, except for specialized applications, they would all pale in their sensitivity compared to what fluorescence could offer. It is therefore likely that atomic fluorescence, not AAS, would benefit most greatly from the availability of an "ideal" laser for atomic spectrometry.

Two other limitations imposed largely by the HCL could be addressed by the same schemes outlined above for implementing multielement AAS. Specifically, multielement capability would dramatically improve the rate of sample analysis in AAS simply by obviating the need to examine each sample repeatedly for the determination of additional elements. Similarly, a truly multielement AAS instrument should be capable of qualitative as well as quantitative analysis. Of course, sample throughput can be enhanced also by a number of automation schemes, most of which are already available commercially. Flow-injection analysis is an especially attractive approach that can be used effectively to help automate AAS and to speed both calibration procedures and sample determinations.

Atomizer-Related AAS Shortcomings

The fact that AAS is ordinarily performed in a single-element mode is attributable in part also to the use of furnace atomizers. Furnace atomizers, even more than chemical flames and far more than high-temperature, rare-gas plasmas (e.g. the ICP) require the separate optimization of conditions for each element to be determined. Many attempts to use furnaces in a multielement mode have resulted in serious losses of the more volatile elements during the "dry" or "char" periods. Or, under compromise operating conditions, have resulted in incomplete volatilization of the more refractory elements.

Clearly, what would be desired is an AAS atomizer which is capable of the quantitative conversion of a sample into free atoms, which can then be probed for analysis. This capability would also ensure the viability of absolute (standardless) analysis (21) and would minimize or eliminate matrix effects. Lamentably, an atomizer of sufficiently high thermal temperature to guarantee volatilization of all elements in the periodic table would also produce both a large fraction of atomic ions and a rather substantial spectral background. These characteristics would require major changes in AAS instrumentation and might seriously compromise the analytical utility of the technique.

Perhaps what would be better is to employ an atomizer which functions in a non-thermal manner. One such process is rare-gas sputtering. In view of the promise of sputtering-based atom cells in AAS, it is surprising in retrospect to review the excellent work performed some time ago at CSIRO in Australia (see, for example, reference 1). Recently, a modified sputtering-based atomizer has been introduced in the marketplace (14) which offers many of the same capabilities. This new system (14), unlike earlier sputtering

chambers, operates in a mode in which the conventional gas flows are reversed in direction. Incoming inert gas (argon) is directed at the sample surface, so the redeposition of sputtered material is minimized. Also, this altered gas-flow configuration produces above the sample surface an unusually high concentration of sample atoms, a situation which is intentionally avoided in emission measurements. However, like glow-discharge lamps designed for emission spectrometry, the new system produces after an initial equilibration time an atom population which is representative of the sample being examined. Consequently, matrix effects are minimized and samples having a range of composition can be analyzed with the same working curve (22).

Another attractive but somewhat less satisfactory approach to "universal" multielement AAS is to identify a matrix modifier which would perform satisfactorily in furnace AAS for all elements and most samples. To date, no such universal matrix modifier has been found, although Pd offers some promise (23).

Incomplete atomization of samples is responsible not only for the problems outlined above, but also for the need to incorporate background-correction facilities into AAS instrumentation. As many others have noted, background correction is especially important when furnace atomizers are employed.

In the past few years, a controversy has existed whether Zeeman-based background correction or correction based on pulsed hollow cathodes (the so-called Smith-Hieftje method) is superior. In large part, an individual advocating one approach over the other has not been entirely disinterested and commonly represented an instrument company that offered the particular approach being promoted. More objective and independent appraisals (see,

for example, 24-26) have shown that both techniques perform admirably and appear to be superior to deuterium-lamp-based correction procedures.

Another attractive option for overcoming background absorption or scattering is to employ the atomic magneto-optic-rotation (AMOR) effect. The resulting analytical method, commonly called coherent forward scattering (CFS) spectrometry, can be implemented in a fashion (27,28) in which background absorption does not contribute to the measured signal.

In CFS, atoms contained within a magnetic field are capable of rotating the plane of polarization of light that passes through them. Importantly, the extent of this rotation is dependent only on fundamental properties of the atoms, on their concentration, on the pathlength of light through the atoms, and on the strength of the enclosing magnetic field. If the intensity of the primary light source changes, or if background absorption or scattering occurs, the intensity of the transmitted radiation will be affected, but the angle through which the polarization is rotated will not.

A convenient way of gauging this angular rotation is by means of polarization modulation. With such an approach, extremely small rotation angles can be determined by means of phase measurements, so that achievable sensitivity and detection limits rival those offered by conventional graphite-furnace AAS (28).

Sample-Form Flexibility. As stated earlier, development of a truly attractive multielement AAS system will require modification or replacement of current atomizers. As a result, it might be possible also to achieve greater flexibility in the form samples must take. At present, of course, solution samples are almost exclusively employed in routine AAS. However, with the introduction of sputtering-based atom cells, it will be possible to employ solid samples directly.

Ideally, one would wish to utilize the same atomizer for samples in solid, liquid, or gaseous states. Some improvements have recently been made in the introduction of slurries into furnaces (29), but such approaches are far more attractive when coupled with higher-temperature atomizers.

A host of other atomizers have been applied to solid-sample analysis, including a high-voltage spark, alternative furnace configurations, and cells that employ laser ablation. Regardless, from a practical standpoint, a sputtering-based atom cell seems far more appealing.

Methods for Increasing Linear Range

AAS, by its very nature, ordinarily exhibits a linear dynamic range between 100 and 1000. That is, unlike many competitive approaches (e.g. ICP emission), it is necessary to employ several sample dilutions in order to cover the range of elemental concentrations found in a typical sample.

Several alternatives have been proposed for extending the dynamic range in AAS. The only one possible with commercial instrumentation, at the present time, is the use of multiple magnetic fields in Zeeman-modulation AAS (30). In essence, the use of Zeeman splitting enables the measured portion of an atomic spectral line to be shifted somewhat, so its absorptivity (absorption coefficient) is diminished. As a result, the measured absorbance falls within the dynamic range of which the instrument and method are capable.

Another attractive routine is possible if a continuum source and high-resolution spectrometer are employed (31). With this combination, in a manner similar to that employed during multiple-field Zeeman modulation, measurements can be taken on the wings of an atomic line, where absorbances

are lower. Dynamic range is thereby extended by two or more orders of magnitude.

A similar concept could be implemented on systems that employ the pulsed-HCL approach to background correction. Just as in multiple-field Zeeman modulation, it would be possible to utilize several different levels of operating current in an HCL to broaden the lamp's spectral profile to differing degrees. Several working curves would thereby be generated (32) and dynamic range correspondingly increased. To the author's knowledge, this latter approach has not yet been investigated experimentally.

Where Do We Stand?

At this point, it is appropriate to review the foregoing comments in an effort to ascertain whether a modified AAS instrument can be envisioned which improves on current technology. It is tempting to suggest that continuum-source AAS, coupled with a sputtering-based atomizer, a high-resolution spectrometer, and a state-of-the-art imaging detector would offer greatly enhanced capability over present systems. But such a system would still suffer from relatively low radiant power at short wavelengths and would provide no intrinsic wavelength lock to the atomic lines of interest. Thus, it might be necessary to employ two sources and to incorporate a highly stable, internal calibration system.

Unfortunately, even with these additions, it is unlikely that AAS would surpass in overall capability those techniques with which it is now competitive. Detection limits in ICP-mass spectrometry are already at a level equivalent to those offered by graphite-furnace AAS and are likely to improve in the future. Further, both ICP-MS and the corresponding emission technique generate minimal interelement interferences, provide a broad

dynamic range, and offer inherent multielement capability. In addition, detection limits in AAS, especially those obtained with a continuum source, fundamentally cannot surpass those attainable with atomic fluorescence or emission, which are naturally more oriented toward multielement detection (33). We are therefore left in the position that AAS seemingly cannot be improved markedly beyond its current capability. At present, AAS is still a simple-to-use, relatively inexpensive method for the routine, automated single-element analysis for samples of various kinds. Any attempt to improve its capabilities (to offer multielement determination, qualitative-analysis capability, or to improve the atomizer) will no doubt increase its cost and complexity. These changes will, in turn, place the method into more direct competition with those based on emission, mass spectrometry, or possibly fluorescence. In the resulting comparison, AAS will almost certainly suffer.

What, then, does the future hold for AAS? Is its age of senescence already here? Will it be utilized only in undergraduate experiments and in small laboratories? Or will it be employed mainly as a diagnostic device in more fundamental or specialized measurements? Indeed, the recent introduction of low-cost ICP instruments makes even these future applications seem questionable.

The Possible Future--A Glimpse

Several possible areas of improvement for AAS exist, the previous comments notwithstanding. For example, there will probably be continuing attempts to employ AAS for isotope determination of both light and heavy elements, especially when reduced-pressure atom reservoirs are employed. Under reduced-pressure conditions, spectral lines are narrowed because

collisions are reduced and, under appropriate expansion conditions, atoms are cooled. As a result, collisional and Doppler broadening are both diminished. Isotopically enriched spectral lamps (electrodeless or HCL) could then be used for selective determination of isotopes by AAS.

It is clear that continued and progressive "computerization" of commercial instrumentation will continue. To date, the computers added to such instruments have served principally to make life simpler but less secure for the operator. In a modern AA spectrometer, an automated "cookbook" is made available to the user. Selections involving elements to be determined, sample type, sample order, and other matters are all selected from a predefined menu. In some situations, manual controls have been removed entirely from the face of the instrument, so the operator need not concern himself with how well the instrument is operating or with the adjustment of most parameters.

In the future, we might hope for something better and less unimaginative. It would be desirable to have feedback signals provided by the instrument itself to enable a controlling computer to improve analytical conditions during the course of an analysis. Indeed, the computer and instrument should interact in an iterative fashion to improve the conditions of an analysis. Ideally, it should be possible in this way to optimize all experimental conditions the first time a determination is performed. It might therefore be possible to improve detection limits and precision and offer interference-free determinations. Of course, this "adaptive optimization" approach could also be employed with competitive atomic spectrometric methods and would improve them as well. In all cases, it will then be necessary to devise rapid, microsampling techniques so that a sample can be rapidly examined, conditions altered to improve the determination,

and the measurement procedure procedure repeated. Conveniently, appropriate repetitive microsampling techniques are already available for this purpose (34).

Alternative methods for background correction will also certainly become available. An interesting and attractive concept would involve the microwave modulation of radiation from an HCL. Whether the modulation would take place within the HCL itself or by means of an external device, it would produce sidebands which would surround the atomic line (see Figure 4). That is, if the primary atomic spectral-line radiation were at an optical frequency ν_0 , the sidebands would exist at $\nu_0 + \nu_m$ and $\nu_0 - \nu_m$, where ν_m is the microwave-modulation frequency. With appropriate selection of ν_m , the sidebands could examine the spectral background on both sides of an atomic line and at a selectable spectral displacement from that line.

It is certain that AAS will continue also as a diagnostic tool and possibly as a device to enhance the capability of alternative spectrometric techniques. For example, it was mentioned earlier that the selective spectral-line modulation approach requires the use of atomic absorption to achieve its spectral selectivity (20). Also, fundamental studies of atoms will depend upon the absorption of photons from high-powered lasers. Using such sources, it has recently been shown possible to "cool" atoms to temperatures near absolute zero and to trap them in a potential well created by an imposed radiation field. In essence, an atom is cooled (slowed in velocity) by absorption of photons traveling in the opposite direction. The absorbed photons impart their momentum to the atom and reduce its velocity; any fluorescence which results will be emitted isotropically and, on balance, will not greatly affect this velocity change. Once the atom has slowed sufficiently, it can be trapped in a light-wave field by selecting

counterpropagating laser beams whose frequencies are shifted slightly from the atomic absorption line. If the atom attempts to move in the direction of either laser, it generates a Doppler shift that places its absorption line in resonance with the impinging photons. As a result, the photons are absorbed and the atom is stopped.

These developments are undeniably interesting and of possible future importance to analytical atomic spectrometry. However, what of the immediate future of AAS as a routine analytical method? Let us return briefly to Fig. 1, where the number of publications describing AAS is charted. It is always tempting in assessing any such plot to determine whether the observed behavior follows a mathematical model. For the data displayed in Fig. 1, a third-order polynomial fits quite nicely and is shown in Fig. 5. The curved line displayed in Fig. 5, which has a squared correlation coefficient (r^2) of 0.967, suggests that publications in AAS are already in rapid decline and should drop to zero before the year 2000. Although this sort of behavior can hardly be viewed with confidence and is offered here with tongue in cheek, the statistical agreement is remarkable. All facetiousness aside, the foregoing analysis argues that AAS as we now know it is indeed on the descent. I believe this trend will continue unless new developments, now unforeseen, take place. With the currently rapid growth in ICP-emission and ICP-mass spectrometry and with new incursions being made by methods based on glow-discharge lamps, AAS is bound for difficult times. If current trends continue, I would not be surprised to see the removal of commercial AAS instruments from the market place by the year 2000.

Acknowledgement

This work was supported in part by the National Science Foundation through Grant CHE 87-22639, by the Office of Naval Research, and by the American Cyanamid Company.

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Table 1. Key Events in AAS

Background Developments

(Up to 1930)

- 1752 Thomas Melville - notes yellow flame arises from sea salt**
- 1802 Wollaston - observes 7 dark lines in solar spectrum**
- 1817 Josef Fraunhofer - records 590 dark lines in solar spectrum**
- 1826 W. H. F. Talbot - relates color of flame to specific added substances**
- 1860 Kirchhoff and Bunsen - Flame photometry; I.d. of Fraunhofer lines as AA**
- 1876 L. G. Gouy - nebulizes samples into flame**
- 1878 Lockyer - coke-fired furnace for AAS**
- 1916 F. Paschen - description of HCL**
- 1928 Lundegårdh - premix air/C₂H₂; pneumatic nebulizer; spray chamber; automation**

Table 2. Key Events in AAS

Firsts

(1940-1960)

- 1941 Ballard & Thornton - det'n of Hg in lab air by AAS**
- 1953 A Walsh - first patent in AAS**
- 1954 Brody, et al. - first isotope analysis by AAS (Li)**
- 1955 A. Walsh and C. T. J. Alkemade - first papers in "modern" AAS**
- 1958 First papers on applications of AAS**
- 1959 L'Vov - First paper on Graphite-furnace AAS**
- 1961 L'Vov's paper appears in English**
- 1961 Elwell & Gidley - first book on AAS**

Table 3. Key Events in AAS

Instrument Developments

(1961 to Present)

- 1965** Amos & Willis - introduction of $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ flame
Koirtyohann & Pickett - D_2 background correction
- 1968** Massman - "practical" graphite furnace for AAS
- 1969** Holak - hydride-generation methods
- 1971** Hadeishi & McLaughlin - Zeeman-based background correction
- 1973** Church & Hadeishi - Use of Coherent Forward Scattering for analysis
- 1977** Constant-temperature furnaces introduced commercially
- 1983** Smith-Hieftje background correction

Table 4. Ideal Multielement Method of Analysis

- *High sensitivity (ppb-ppt)*
- *Broad linear dynamic range*
- *High precision (0.1%)*
- *No matrix interferences*
- *Inexpensive (initial and operating)*
- *Useful for all elements under the same operating conditions*
- *Ease of choice of elements to be determined*
- *Simple to operate*
- *Compact instrument*
- *Minimal sample preparation (gases, liquids, solids)*
- *Microsampling capability*
- *Rapid (per sample/ per element)*
- *Non-destructive*
- *Amenable to automation*
- *Self-diagnosing*

Figure Captions

- Figure 1. Publications cited in Chemical Abstracts over the period 1967-1987.
- Figure 2. Schematic diagram illustrating the resonance Schlieren process and how it can be used for atomic spectrometry. Ordinarily, Schlieren measurements enable refractive-index gradients in a probed volume to be mapped. A. Collimated light passing through the probed volume (atom cell, here) deviates from its original direction when it encounters a refractive-index gradient. As a result, it bypasses a knife edge that blocks the focal point of the originally collimated beam. Because anomalous dispersion (B) produces a substantial refractive-index gradient at wavelengths corresponding to an atomic transition, the Schlieren process is much more dramatic at wavelengths near the line. Consequently, a large fraction of the radiation detected in resonance Schlieren spectrometry is attributable to atomic spectral-line radiation. This feature helps to overcome contributions from broadband sources and could be used for multielement AAS.
- Figure 3. When two collimated beams derived from the same laser (at wavelength λ) are allowed to cross within an atom-containing medium, they develop an interference pattern. If λ corresponds to an atomic transition, the regions of

constructive and destructive interference produce a spatially modulated excitation pattern in the atoms which, through thermal relaxation, can generate a thermal grating. A probe beam, oriented in a direction orthogonal to the induced grating, will then be deflected by an amount that depends upon the power in the original collimated beams and on the atomic concentration. Although not practicable for routine AAS determinations, this induced-grating effect is useful for mapping the spatial features of analytical sources.

Figure 4. A hollow cathode lamp (HCL) spectrum consists ideally of a single line, portrayed on the left. If the lamp or radiation emanating from it were modulated at sufficiently high (e.g. microwave) frequencies, side-bands would appear in the resulting optical spectrum (right side). These side bands would be useful in examining the spectral region adjacent to an atomic line of interest and would therefore be useful for AAS background correction.

Figure 5. A third-order polynomial, when fitted to the data in Fig. 1, suggests that AAS publication should drop to zero before the year 2000. The square of the correlation coefficient (r^2) for this line is 0.967.

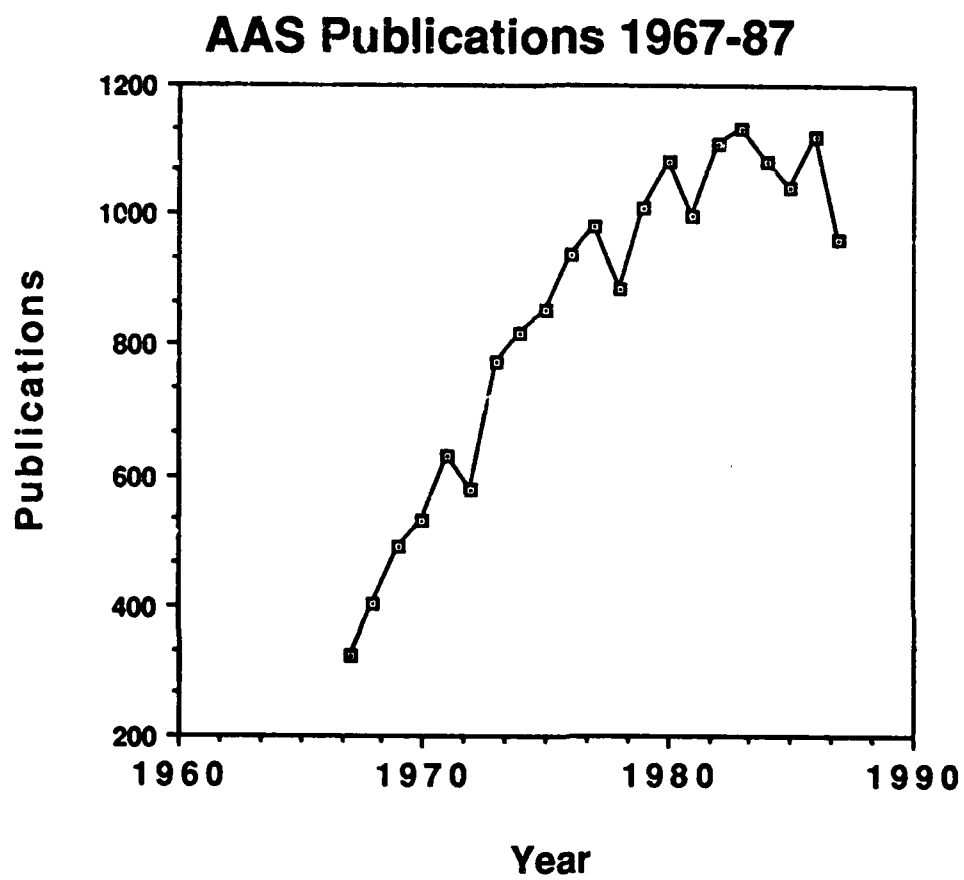
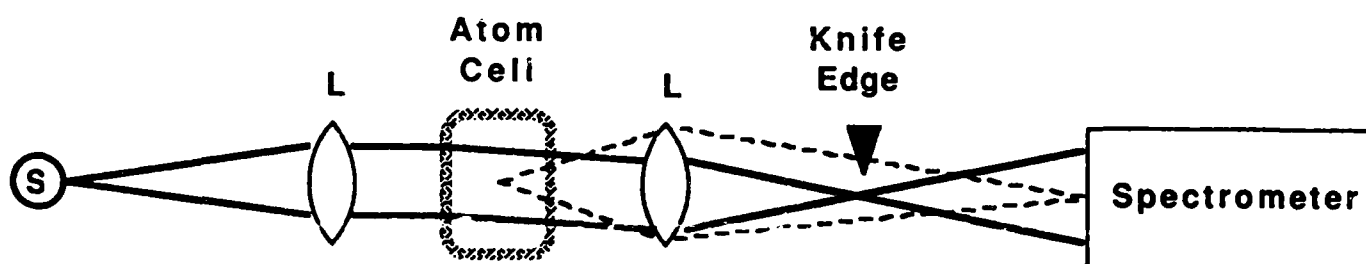
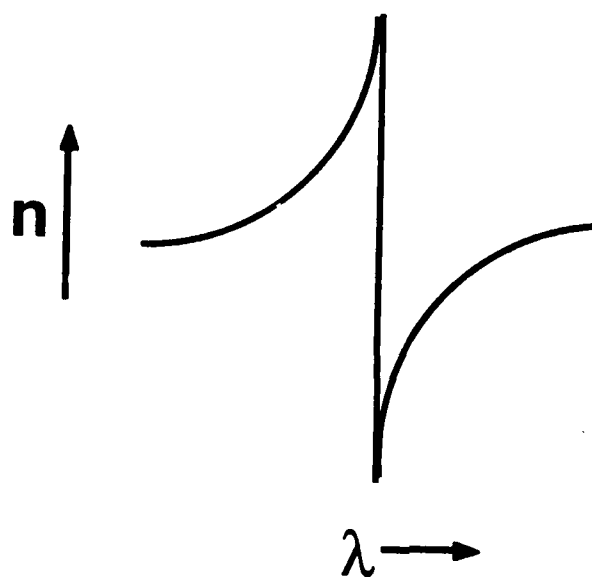


Fig. 1



Resonance Schlieren Spectrometry

Fig 2A



**Anomalous
Dispersion**

Fig. 2B

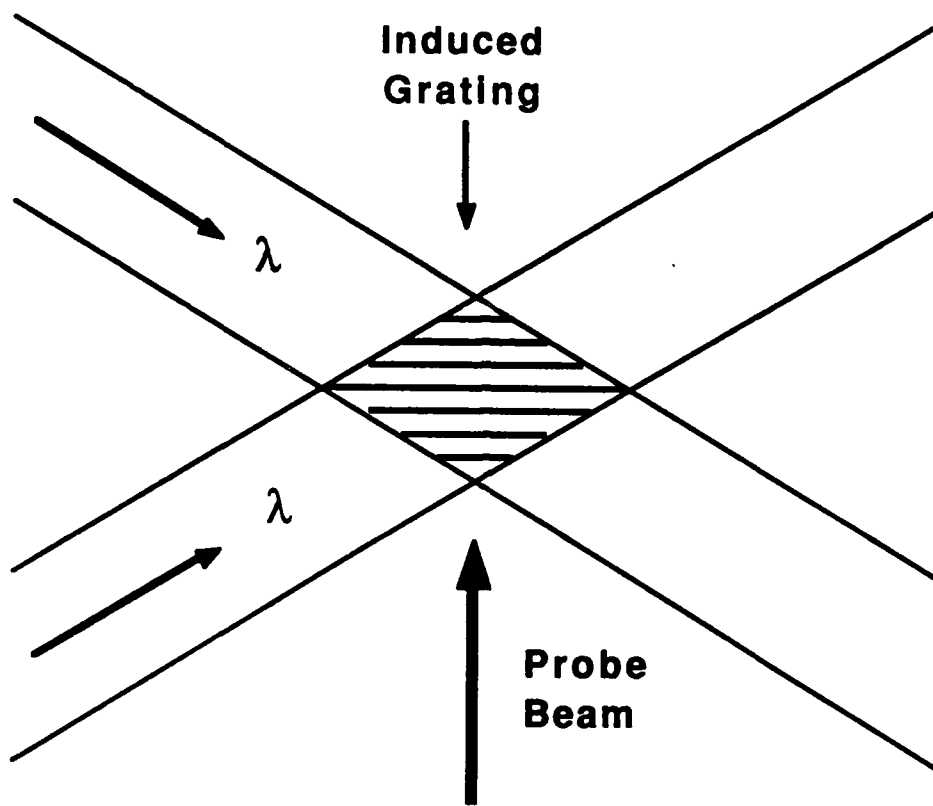


Fig. 3

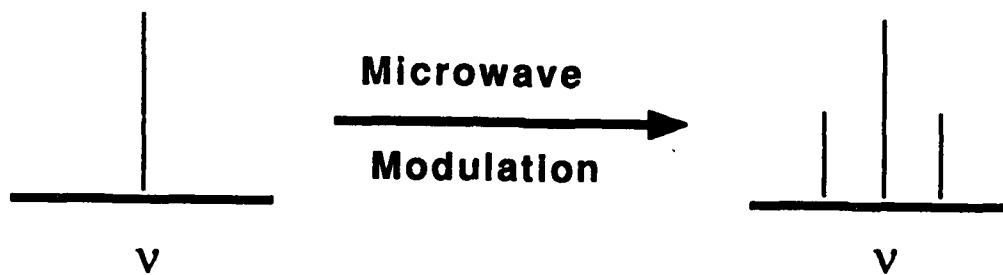


Fig. 4

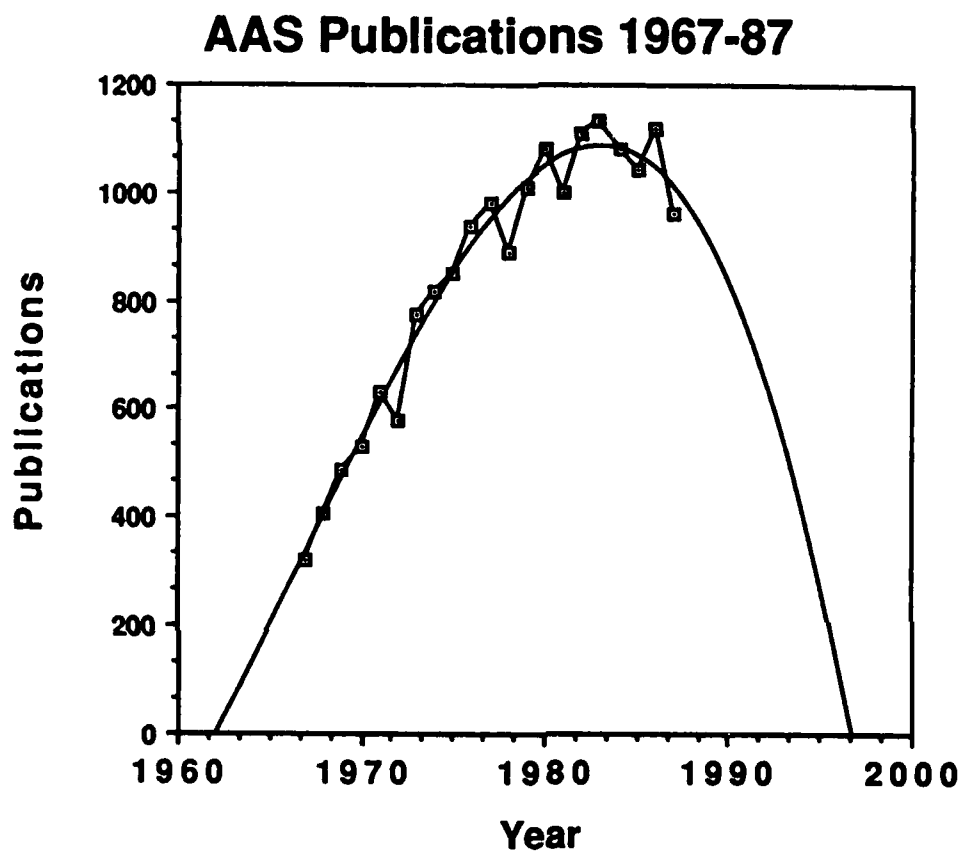


Fig. 5

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